

DIDEUTERIUM INCORPORATION DURING THE COPROCESSING REACTION OF LLOYDMINSTER PETROLEUM RESID AND ILLINOIS NO. 6 COAL IN D₂

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INTRODUCTION

Coal petroleum resid coprocessing is fast becoming a cost effective means of coal liquefaction. The reaction mechanisms, however, are not well understood and are very important to the development and improvement of the technology. The coprocessing reaction is carried out at high temperatures and under a dihydrogen atmosphere that donates hydrogen to the fossil fuels to provide higher yields of liquids and to increase their hydrogen content. Accordingly, we have undertaken a study of the role of dihydrogen in the coprocessing reaction. The initial research in which Illinois No. 6 coal or Wyodak coal and Lloydminster resid or Hondo resid was mixed with a molybdenum based UOP proprietary catalyst was carried out under a 3000 psi dideuterium atmosphere at 420°C with a heat up time of 120 minutes and a residence time of 120 minutes¹. Quantitative 1H and 2H NMR analyses yielded similar results for the four combinations of coals and resids. Specifically, the degree of deuteration, (D/H+D), of the coprocessed products approached 0.25, the value that was expected for complete equilibration of the isotopes among the available positions in the oil, resin, and asphaltene. These results established the unselective character of the severe coprocessing reaction. However, we sought information on the limiting processes. Accordingly, additional coprocessing reactions with Illinois No. 6 coal and Lloydminster resid have been carried out under less severe conditions to investigate how the dideuterium utilization in the reaction products is affected by changes in the temperature and pressure.

EXPERIMENTAL

Materials. Illinois No. 6 coal was prepared by the Kentucky Center for Energy Research (KCER) and used as received (Anal. %C, 68.60; %H, 4.51; %N, 1.39; %S, 3.04; %O, 9.65; %H₂O, 3.15; %Ash, 9.65). Lloydminster Resid (Anal. %C, 83.6; %H, 11.5; %S, 4.77; %N,) was obtained by UOP Research Center and used as received. The catalyst used was a molybdenum based UOP proprietary catalyst.

Coprocessing Reaction Procedure. Weighed amounts of Lloydminster and Illinois No. 6 coal in a two to one ratio (resid/MAF coal) and the catalyst (2%wt) are added to an 1800ml rocking autoclave. The autoclave is sealed and is pressurized first with hydrogen sulfide and then with dihydrogen or dideuterium to give a 10 vol% hydrogen sulfide and 90 vol% dideuterium such that the desired pressure is obtained at reaction temperature. The autoclave is heated to the desired temperature for a residence time of 0.0, 0.5, or 2 hours. At the reaction conditions, dideuterium is added automatically so that the desired reaction pressure (1770 or 3000psi at temperature) is maintained. After the desired time-at-temperature, the autoclave is cooled to room temperature, and is then depressurized with the gas passing through a foam trap, caustic scrubbers, metering system, and then a sample is collected for analysis. To remove additional gas from the remaining reaction mixture, the material in the autoclave is stripped with dinitrogen. This gas also is passed through the foam trap, caustic scrubber, metering system, and analyzed. Any slurry product recovered in the foam trap is recovered with toluene and added to the toluene rinse solution. The slurry product from the autoclave is decanted. The material that remains in the autoclave is removed by rinsing the vessel with toluene until the autoclave is clean. The combined slurry

product is solvent separated into four fractions (oil, resin, asphaltene, and insoluble) according to a previously reported procedure¹.

Analysis. Deuterium spectra were obtained on a Varian XL 400 MHz spectrometer. Two hundred fifty six scans were acquired by using a 90° pulse and a .5 second delay between pulses. Benzaldehyde- α -d-1 was used as a quantitative internal standard. Proton spectra were obtained similarly on the same instrument by using a 90° pulse and a 20 second delay between pulses. Elemental analyses for carbon and hydrogen for each solvent separated product were obtained from Huffman Laboratories by using an instrument that detected both hydrogen and deuterium².

RESULTS

The autoclave reactions were carried out with Illinois No. 6 coal, Lloydminster resid and a molybdenum based UOP proprietary catalyst. Temperature was varied from 390 to 420°C and pressure was varied from 1770 to 3000 psi of dideuterium. The actual reaction time is a sum of the heat up time, approximately two hours, and the residence time, 0.0, 0.5, or 2 hours. The coprocessed products were solvent separated into four fractions; oil (isopentane soluble), resin (heptane soluble-isopentane insoluble), asphaltene (toluene soluble-heptane insoluble), and insolubles (toluene insoluble). The yields of each fraction, the coal conversion, and the asphaltene conversion for each reaction are provided in Table I.

The solvent separated products were quantitatively analyzed by proton and deuterium NMR methods and elemental analysis. The NMR spectra were partitioned into regions: aromatic resonances (12.0 - 6.0 ppm), total aliphatic resonances (5.0 - (-2.0) ppm), alpha aliphatic resonances (5.0 - 2.0 ppm), beta aliphatic resonances (2.0 - 1.0 ppm), and gamma aliphatic resonances (1.0 - (-2) ppm). Hydrogen content, deuterium content, and % deuteration at each position in the oil, resin, and asphaltene fractions were determined as shown in Table II, and (H+D)/C ratio is shown in Figure 1.

The data in Tables I and II clearly show the effects of temperature and pressure on the yields and conversions in the coprocessing reaction. Temperature proves to be the dominant driving force for conversion. An increase in dideuterium pressure from 1770 to 3000 psi at 390°C has essentially no effect on either coal or asphaltene conversion, or on the yields of any of the solvent separated products. However, except for the aromatic positions, an increase in pressure does increase the deuteration at all positions, and the (H+D)/C ratio increased in the oil, resin, and asphaltene fractions. Aromatic deuteration increased from 17.2 to 19.1%, mainly in the resin and asphaltene fractions. The increase in aliphatic deuteration from 9.1 to 12.1% was dominated by incorporation at the alpha position.

An increase in reaction temperature from 390 to 405°C and then to 420°C had a dramatic effect on the coal and asphaltene conversions. The coal conversion increased from 42.6 to 75.0% at 405°C, and then to 92.1% at 420°C. The coal conversion reached its maximum of about 92% at 420°C with no residence time. The same result was realized both when the residence time was 0.5 hours and 2.0 hours. The asphaltene conversion steadily increased from 13.0 to 29.6% at 405°C, and then to 40.1% at 420°C. The oil and asphaltene yields increased slightly, but most importantly the insoluble yield decreased significantly from 19.3% at 390°C to 2.7% at 420°C enabling the high coal conversions. In addition, the increase in temperature from 390 to 405°C, and from 405 to 420°C provided almost linear increases in deuteration at all positions. Approximately 9-10% increases are seen in the deuteration of all the aliphatic positions in the oil, resin, and asphaltene fractions with the exception of the alpha position in the resin and asphaltene fractions. The lack of a comparable increase in alpha % deuteration is almost certainly the result of the already high level

of deuterium incorporation in the alpha position at 390°C. Increases in the aromatic region averaged about 7.5%.

Both coal conversion and alpha D exchange reach their maximum at 420°C with no residence time. As the residence time was increased, coal conversion remained constant and % alpha deuteration declined in all three fractions while the asphaltene conversion exhibited its largest increase. As the residence time and, consequently, the asphaltene conversion were increasing, the % aliphatic and % overall deuteration remained essentially constant in the asphaltene fraction while the % aromatic deuteration and the % alpha deuteration decreased. The increase in % deuteration in the beta and gamma positions compensated for the decreases in the other positions to keep the overall % aliphatic deuteration of the asphaltene fraction constant indicating the approach to equilibrium of H and D in the asphaltenes. The alpha position was still slightly favored.

However, as the residence time at 420°C is increased, the % deuteration at the other positions (aromatic, beta, and gamma) in all three fractions increases, and lead to an increase in the overall aliphatic and total deuteration in the oil and resin fractions. In addition, (H+D)/C significantly decreases in the resin and asphaltene, and to some extent in the oil.

CONCLUSIONS

Increasing pressure and temperature both lead to increased deuterium uptake from the dideuterium atmosphere. Temperature is, however, the driving force behind the conversion chemistry. Deuterium uptake, asphaltene conversion, and coal conversion all increase as temperature is raised from 390 to 420°C. Once 420°C is reached, coal conversion chemistry and % alpha deuteration have reached their maximum levels. As residence time at 420°C is increased, the chemistry responsible for increased asphaltene conversion and the upgrading of these asphaltenes to resins and then to oils takes place. The initially high levels of deuterium atoms in the alpha positions decrease as reactions at the less reactive beta and gamma positions occur. The deuteration at all sites in the asphaltene fraction essentially remains constant at about 27% as residence time at 420°C is increased, but the (H+D)/C ratio decreases as the asphaltene conversion and upgrading of asphaltenes to resins and oils takes place. Concurrently, (H+D)/C is also decreasing in the oil and resin. However, the overall deuterium uptake is still increasing from 18.6 to 26.7% in the oil, and from 23.9 to 30.9% in the resin.

REFERENCES

1. Ettinger, M.; Stock, L. M.; Gatsis, J. G.; Prepr. Pap. - Am. Chem. Soc., Div. Fuel Chem. 1991, 36(2), 635.
2. Total %wt H+D was calculated by correcting the elemental analysis %wt H using quantitative deuterium values provided by NMR analysis. The calculation can be found in the dissertation of Michael D. Ettinger, University of Chicago Libraries.

Table I. Reaction Conditions, Yields (wt%MAF), and Conversions (wt%MAF)

Conditions	Oil	Resin	Asphaltene	Insolubles	Recovered Products	Coal Conversion	Asphaltene Conversion
0.0 hr at 390, 1770psi	53.4	3.8	17.1	18.9	93.2	43.3	15.1
0.0 hr at 390, 3000psi	54.1	3.3	17.7	19.3	94.4	42.6	13.0
0.0 hr at 405, 3000psi	59.7	1.1	21.2	8.3	90.3	75.0	29.6
0.0 hr at 420, 3000psi	55.4	3.6	22.8	2.7	84.5	92.1	40.1
0.5 hr at 420, 3000psi	60.8	1.7	19.3	2.7	84.4	91.9	47.3
2.0 hr at 420, 3000psi	62.3	3.9	8.5	2.4	77.1	92.8	74.2

Figure I. (H + D) / C

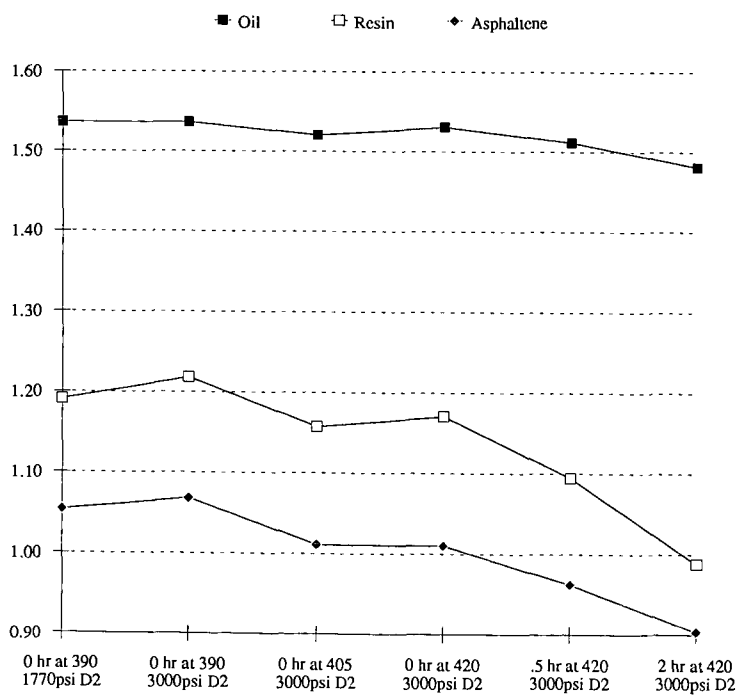


Table II. % Deuteration in Solvent Separated Products

Conditions	Oil	Resin	Asphaltene	Total
<u>% TOTAL D 12.0 - 6.0 & 5.0 (-2) PPM</u>				
0.0 hr at 390, 1770psi	6.59	10.33	14.76	10.03
0.0 hr at 390, 3000psi	8.60	13.97	17.95	12.89
0.0 hr at 405, 3000psi	13.05	17.75	24.43	17.62
0.0 hr at 420, 3000psi	18.57	23.88	27.89	22.78
0.5 hr at 420, 3000psi	20.33	25.07	26.67	23.55
2.0 hr at 420, 3000psi	26.70	30.88	27.59	28.17
<u>% AROMATIC D 12.0 - 6.0 PPM</u>				
0.0 hr at 390, 1770psi	13.28	16.30	20.38	17.23
0.0 hr at 390, 3000psi	13.25	19.10	22.69	19.14
0.0 hr at 405, 3000psi	16.97	22.05	27.42	23.00
0.0 hr at 420, 3000psi	22.50	26.22	29.47	26.70
0.5 hr at 420, 3000psi	22.00	25.47	26.58	25.18
2.0 hr at 420, 3000psi	25.30	31.25	26.66	28.12
<u>% ALIPHATIC D 5.0 - (-2.0) PPM</u>				
0.0 hr at 390, 1770psi	6.09	9.42	13.58	9.06
0.0 hr at 390, 3000psi	8.26	13.25	16.99	12.08
0.0 hr at 405, 3000psi	12.72	17.04	23.70	16.82
0.0 hr at 420, 3000psi	18.23	23.40	27.46	22.11
0.5 hr at 420, 3000psi	20.17	24.98	26.70	23.23
2.0 hr at 420, 3000psi	26.85	30.75	27.97	28.18
<u>% ALPHA D 5.0 - 2.0 PPM</u>				
0.0 hr at 390, 1770psi	19.38	21.30	25.27	22.09
0.0 hr at 390, 3000psi	25.14	29.41	30.36	28.46
0.0 hr at 405, 3000psi	29.63	31.65	34.42	32.02
0.0 hr at 420, 3000psi	36.29	35.44	36.52	36.06
0.5 hr at 420, 3000psi	35.61	34.35	33.64	34.45
2.0 hr at 420, 3000psi	34.27	35.01	31.69	33.68
<u>% BETA D 2.0 - 1.0 PPM</u>				
0.0 hr at 390, 1770psi	3.82	5.14	8.25	5.19
0.0 hr at 390, 3000psi	5.43	7.54	10.25	7.15
0.0 hr at 405, 3000psi	9.65	11.30	16.96	11.62
0.0 hr at 420, 3000psi	15.85	17.48	21.20	17.41
0.5 hr at 420, 3000psi	18.72	20.31	21.39	19.70
2.0 hr at 420, 3000psi	27.35	28.61	24.74	27.13
<u>% GAMMA D 1.0 - (-2.0) PPM</u>				
0.0 hr at 390, 1770psi	2.48	5.25	8.47	4.87
0.0 hr at 390, 3000psi	3.26	7.54	11.32	6.54
0.0 hr at 405, 3000psi	6.86	11.57	18.36	11.11
0.0 hr at 420, 3000psi	9.86	16.26	21.72	14.16
0.5 hr at 420, 3000psi	11.56	17.98	22.72	15.54
2.0 hr at 420, 3000psi	18.70	24.19	25.35	21.25